

Starch Graft Poly(methyl acrylate) Loose-Fill Foam: Preparation, Properties and Degradation[†]

L. Chen,[‡] S. H. Gordon,[§] and S. H. Imam^{*,||}

Owens Corning Science & Technology Center, 2790 Columbus Road, Route 16,
Granville, Ohio 43023-1200, Plant Polymer Research Unit, National Center for Agricultural Utilization
Research, ARS-USDA, 1815 North University Street, Peoria, Illinois 61604, and Bioproduct Chemistry and
Engineering Research, Western Regional Research Center, PW-ARS-USDA, 800 Buchanan Street,
Albany, California 94710

Received October 16, 2003

Starch graft poly(methyl acrylate) (S-g-PMA) was prepared by ceric ion initiation of methyl acrylate in an aqueous corn starch slurry (prime starch) which maximized the accessibility of the starch for graft polymerization. A new ceric ion reaction sequence was established as starch–initiator–methyl acrylate followed by addition of a small amount of ceric ion solution when the graft polymerization was almost complete to quench the reaction. As a result of this improved procedure, no unreacted methyl acrylate monomer remained, and thus, essentially no ungrafted poly(methyl acrylate) homopolymer was formed in the final grafted product. Quantities of the high purity S-g-PMA so prepared in pilot scale were converted to resin pellets and loose-fill foam by single screw and twin screw extrusion. The use of prime starch significantly improved the physical properties of the final loose-fill foam, in comparison to foam produced from regular dry corn starch. The S-g-PMA loose-fill foam had compressive strength and resiliency comparable to expanded polystyrene but higher bulk density. The S-g-PMA loose-fill foam also had better moisture and water resistance than other competitive starch-based materials. Studies indicated that the starch portion in S-g-PMA loose-fill foam biodegraded rapidly, whereas poly(methyl acrylate) remained relatively stable under natural environmental conditions.

Introduction

Incorporation of starch with synthetic polymers will reduce the demand on our precious petroleum resources, assist the degradation of plastic end products, and add value to our excessively produced farm products.

Use of granular starch as filler in plastics began with the work of Griffin,^{1–3} in which up to 10% of dry starch was added to the synthetic plastics. Silanes were applied in the starch surface treatment to increase the compatibility of hydrophilic starch with the hydrophobic plastic matrix. At about the same time, Otey and co-workers^{4,5} initiated investigation on blending gelatinized starch with hydrophilic synthetic polymers. Blown films were obtained from mixtures of starch and poly(ethylene acrylic acid) in the presence of aqueous ammonium hydroxide and urea.⁶ Addition of hydrophilic poly(vinyl alcohol) to this blend of materials increased the tensile strength and showed little effect on the

elongation.⁷ This type of starch-hydrophilic synthetic polymer composites were further developed and marketed by Warner-Lambert.⁸

Starch-based thermoplastics can also be prepared by graft polymerization. One such material receiving extensive study is starch graft poly(methyl acrylate) (S-g-PMA). Methyl acrylate monomers were rapidly polymerized and attached to starch in aqueous starch slurry using ceric ammonium nitrate as initiator.^{9–16} The products displayed interesting water absorption and tensile properties.^{9,10} Besides corn starch, potato starch¹⁷ and cereal flour¹⁸ also underwent graft polymerization with methyl acrylate monomer, and similar properties were observed. One potential application suggested for S-g-PMA was as shrinkage blown film¹⁹ where poly(methyl acrylate) contents were around 50%.

One significant advance in the commercialization of starch-based plastics is the rapid growth of the starch-based packaging loose-fill foam market.²⁰ Traditionally, expanded polystyrene (EPS) has been the sole foam packaging material. Two environment concerns of EPS have been raised: its visibility and indestructibility when discarded in landfill and the release of blowing agent, chlorofluocarbon, during processing, which has been proved harmful to the earth's ozone layer. It is estimated that more than 10% of EPS has been replaced by starch-based loose-fill foam, and this rate is steadily increasing as the quality of starch-based materials is improved.

[†] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable. All programs and services of the U.S. Department of Agriculture are offered on a nondiscriminatory basis without regard to race, color, national origin, religion, sex, age, marital status or handicap.

^{*} To whom correspondence should be addressed. Phone: 510-559-5794. Fax: 510-559-5936. E-mail: simam@pw.usda.gov.

[‡] Owens Corning Science & Technology Center.

[§] National Center for Agricultural Utilization Research.

^{||} Western Regional Research Center.

Our efforts in identifying the commercial application of S-g-PMA materials resulted in a new development of a pilot process for the S-g-PMA loose-fill foam production, including resin and end-product manufacture. This paper describes the S-g-PMA resin and loose-fill foam production in pilot scale, characterizes the products, and studies their biodegradation.

Materials and Methods

Prime corn starch (14–15% moisture content) was obtained from Corn Products Company International (Argo, Illinois) and used without further treatment. The Methyl acrylate monomer (containing 15–20 ppm monomethyl ether hydroquinone as a polymerization inhibitor) was purchased from Hoechst Celanese. Ceric ammonium nitrate was from Rohm and Hass. Acetone, tetrahydrofuran, and hydrochloric acid were from Fisher, Sigma, and General Chemical, respectively. Polystyrene standards for molecular weight determination were purchased from Waters.

Graft Polymerization. Graft polymerization of methyl acrylate monomers onto starch was carried out in a 1.36 m³ glass lined reactor. The reactor was equipped with a mechanical stirrer, vacuum system, and a nitrogen supplier. The room temperature reaction process was similar in principle to what was previously reported⁹ and has been modified to substantially shorten the overall reaction time, reduce monomer and homopolymer content, and obtain the appropriate molecular weight of poly(methyl acrylate). After the reaction was completed, the liquid in the mixture was removed by centrifugal filtration, and the dewatered cake was pulverized for resin processing.

Starch Graft Poly(methyl acrylate) Resin and Loose-Fill Foam Production. S-g-PMA resin and loose-fill foam were processed by extrusion. A twin screw extruder (Wegner, TX52) and a single screw food extruder were employed for both the resin and loose-filled foam processes. The pulverized S-g-PMA was mixed and extruded under low temperature (<60 °C) to form partially gelatinized resin. Pellets were obtained through a 25 hole strand die using a die-face cutter followed by hot air-drying. The resin pellets were kept in a closed environment to maintain a moisture content at around 17% (w/w).

S-g-PMA loose-fill foam was prepared by extrusion (single screw or twin screw). The configuration of the twin screw was similar to what was reported by Lin et al.²¹ and was further optimized to enhance mixing capability. The temperature of the barrel was controlled by an oil heating system, and the melting zone temperature was maintained between 110 and 150 °C. The screw speed was set around 200 rpm and varied according to the properties of the resin (pellet size and moisture content). A one hole strand die (3.00 mm in diameter) was employed and the die pressure was controlled at around 3 MPa. The extrudate was forced out of the die and expanded as it left the die. The foam was cut into slightly curved cylindrical pieces averaging 4.5 cm in length and 1.9 cm in diameter by a six-blade die face cutter at a speed around 350 rpm. The product was collected in a 0.4 m³ polyethylene bag and sealed for commercial applications.

Characterization of Poly(methyl acrylate). Total content of poly(methyl acrylate) incorporated within starch was determined by a method similar to that described by Patil and Fanta.¹⁸ S-g-PMA samples (~2.5 g) were heated with 100 cm³ of 0.5 N hydrochloric acid in a 250 cm³ round-bottom flask equipped with a condenser. The mixture was refluxed for 1.5–2.0 h to hydrolyze starch into water soluble dextrose. The undesolved poly(methyl acrylate) was isolated by filtration, washed with water and dried in a circulated air oven to a constant weight. The total poly(methyl acrylate) content was calculated from the weight loss on acid hydrolysis.

Ungrafted poly(methyl acrylate) was separated by acetone extraction. S-g-PMA powder (10 g, ~15% H₂O) was stirred with acetone (100 cm³) for more than 5 h at room temperature. The insoluble S-g-PMA solid was isolated by filtration, dried, and weighed. The ungrafted poly(methyl acrylate) homopolymer content was determined by the weight loss on acetone extraction.

Relative Humidity vs Weight Change of Foams. S-g-PMA loose-fill foam samples were stored in humidity controlled chambers. Relative humidity controlled chambers were set up employing saturated aqueous salts in sealed desiccators according to CRC Handbook of Chemistry and Physics, CRC Press, Boston (1991–1992) and the actual relative humidity readings were taken on hygrometers (Thermo-hygro, Fisher) placed inside the chambers:

solid phase	LiCl·H ₂ O	CaCl ₂ ·6H ₂ O	MgSO ₄ ·7H ₂ O	NaCl	Na ₂ SO ₃ ·7H ₂ O
R.H. (%)	16	25	45	81	98

The weight changes of S-g-PMA loose-fill foam samples were determined by weighing the samples before and after humidity controlled equilibration in the above chambers for over one week.

Resiliency Test. Resiliency tests for S-g-PMA loose-fill foam samples were performed using an Instron Universal Testing System (Instron Corp., Canton, Massachusetts). The test method was described by Shogren.²² A 0.635 cm diameter steel probe was attached to the crosshead of the Instron Testing Machine. The specimen was placed on the base, and the probe was lowered until contact was made and the load reached 0.5 N. The probe was then lowered at 30 mm/min for a distance of 3 mm, held for 60 s, and then raised. Compressive strength was calculated as the maximum load/cross-sectional area of the probe while resiliency was calculated as the load at the end of the 60 s relaxation period/maximum load.

Biodegradation in Aqueous Solution. Into a 250 cm³ autoclaved Ernest flask was added 5.00 g of S-g-PMA loose-fill foam, 100 g of deionized water, 0.5 cm³ of a laboratory consortium of highly amylolytic microorganisms designated as LD 76,²³ and 2 cm³ of ALP Basal medium without agar. The flasks were equipped with spongy foam tops and kept in a cabinet at a constant temperature of 28 °C. The samples were removed from the cabinet periodically for analysis. The solid was isolated by filtration and dried in an circulated air

Table 1. Compost Soil Characteristics

total solids	ash	fatty acids	volatile solids	pH	Kj-N
40.0%	71.0%	27.0 $\mu\text{L/g}$	29.0%	7.94	1.43%

oven until constant weight was obtained. The total weight lost was based on the weight difference before and after biodegradation. Weight change and molecular weight of poly(methyl acrylate) incorporated with starch were analyzed according to the above characterization method. The reducing sugar in the filtrate from the biodegraded mixture was determined on a Bran-Luebbe AutoAnalyzer system using Ferricyanide as oxidizing agent and a UV/Visible detector calibrated with glucose.

Biodegradation in Soil. A closed circuit Micro-Oxymax respirometer system (Columbus Instruments, Columbus, Ohio) equipped with expansion interfaces, condensers, and a water bath was used. About 2.00 g of each sample was mixed with 100 g of compost soil in a sample chamber. Sample chambers were placed in a water bath at a constant temperature of 24 °C and connected to the Micro-Oxymax respirometer. The compost soil used in these studies was analyzed with respect to total solids, volatile solids, ash, pH, fatty acids, and nitrogen (Table 1). The total accumulation of CO₂ resulting from biodegradation was recorded every 10 h. Experiments were conducted over a period exceeding 1450 h.

Gel Permeation Chromatography (GPC). Weight and number average molecular weights were determined on a Waters 501 gel permeation chromatograph using ultra-Styrigel columns and a differential refractometer index detector. Tetrahydrofuran was used as the eluent. Polystyrene standards from Waters were used for calibration to compare relative molecular weights, in lieu of absolute molecular weights in the series of poly(methyl acrylate) samples.

FTIR Spectroscopy. FTIR spectra of samples were obtained using an FTS 6000 FTIR spectrometer (Digilab, Cambridge, CT) equipped with a air-cooled DTGS detector. Samples (1.00 mg) were pressed in KBr disks (300 mg), and absorbance spectra were measured at 4 cm⁻¹ resolution, signal-averaged over 32 scans and baseline corrected.

Results and Discussion

Starch Graft Poly(methyl acrylate). The method for preparing S-g-PMA was first reported by Mino and Kaizerman.²⁴ USDA has conducted extensive investigation on graft polymerization and the physical properties of the grafted products.^{9,10} Traditionally, commercial corn starch was slurried in water and sparged with nitrogen at room temperature, and methyl acrylate was added followed by ceric ammonium nitrate in 1 N nitric acid. This process was found to be difficult when adopted to large scale production using a 1.36 m³ reactor. First, the conversion of monomer to polymer was not 100% completed and small amounts of unreacted methyl acrylate monomer caused severe harm to workers and to the environment. Second, the ungrafted poly(methyl acrylate) homopolymer was high (20–30%) which could adversely affect the physical properties of the final

product. Modification and optimization were developed to address the above-mentioned problems in large scale production.

Prime Starch. Prime starch was employed as the raw material. Prime corn starch is a commercial corn starch slurry used without undergoing a drying process. It is our belief that the drying process increases formation of compact starch granules which prevent methyl acrylate monomers from penetrating into the granules. Prime starch, on the other hand, is more open and loose in structure, which offers better accessibility for methyl acrylate graft polymerization. Significant improvement in the resilience and compressive strength of the final loose fill foam was noticed when prime starch was used, in comparison to that from regular dry corn starch. Two additional benefits of using prime starch were its low cost, 20 cents/kg compared to 27 cents/kg for dry starch, and its perfect pH range (4.0–4.5) for the chemical reaction without additional acid.

Graft Polymerization Reaction Procedure. The graft polymerization reaction procedure was modified from the conventional starch–methyl acrylate–initiator sequence to reduce homopolymer content. When methyl acrylate monomer and ceric ammonium nitrate were stirred together using similar reaction conditions in the absence of starch, poly(methyl acrylate) homopolymer was formed which indicated that the initiation by ceric ion and polymerization of methyl acrylate monomers can take place without starch oxidation. To reduce the formation of homopolymer, it would require more free radicals to be generated from starch before homopolymerization is initiated. A new reaction sequence was established as starch–initiator–methyl acrylate and a small amount of ceric ion solution was added when the reaction was almost complete to quench any unreacted monomers. As a result of this improvement, no methyl acrylate monomer was left unreacted and the homopolymer content was undetectable.

The reaction slurry was neutralized with sodium hydroxide, and the S-g-PMA solid was isolated, dewatered, and rinsed using a centrifugation system. The graft content was varied from 5% to 10% with complete conversion yield. The grafted poly(methyl acrylate) was separated from starch by acid hydrolysis and determined using GPC to have a number average molecular weight (M_n) of 1.58×10^5 , a weight average (M_w) of 4.80×10^5 , and a M_w/M_n of 3.04.

The experimental evidence for the presumption that no unreacted residual methyl acrylate monomer remained was the absence of detectable polymer in the soluble fraction when more prime starch and ceric ammonium nitrate initiator were added to the soluble fraction. This treatment of the soluble fraction produced neither grafted poly(methyl acrylate) nor homopolymer, similar to a solution known to be devoid of methyl methacrylate.

The FTIR spectrum of the S-g-PMA product (Figure 1A) indicates the presence of ester functional groups (~ 1740 cm⁻¹) from poly(methyl acrylate) on the starch backbone in contrast to the absence of ester groups in the ungrafted starch shown by its spectrum (Figure 1B).

Starch Graft Poly(methyl acrylate) Loose-Fill Foam. Pelletizing starch-based resin using a twin screw or single

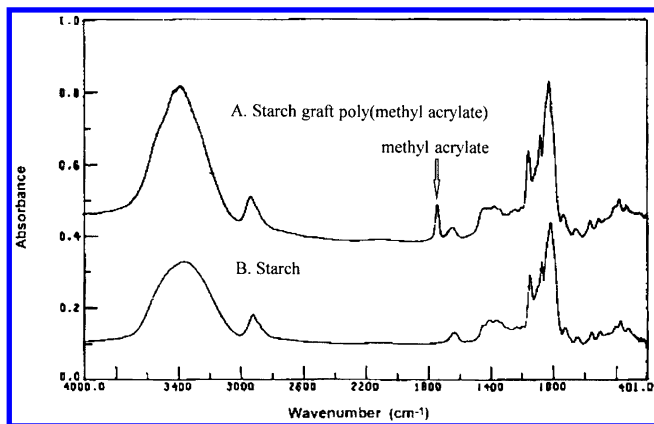


Figure 1. FTIR spectra of starch graft poly(methyl acrylate) (A) and starch (B).

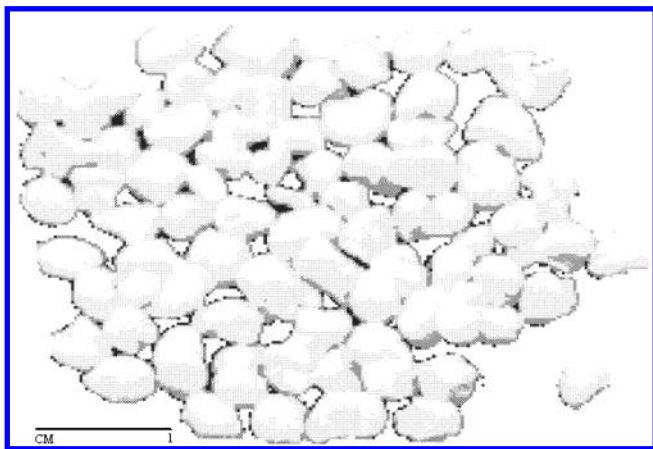


Figure 2. Starch graft poly(methyl acrylate) resin.

screw extruder with one hole strand die in laboratory scale did not present any unusual difficulty. However, when the well gelatinized and tacky starch strands were forced out from a twenty-five-hole die at high speed, they tended to stick to each other, and the separation of strands became impossible. This problem was solved by lowering the extrusion temperature below the gelatinization temperature ($<60^{\circ}\text{C}$) to allow the minimum gelatinization required for pellet formation without tackiness. The extruded strands were cut into cylindrical pieces by a two blade die face cutter with speed ranging from 200 to 300 rpm. The cylindrical extrudates were immediately transferred to a hot air assisted drier to further dewater them and then put into a humidity controlled chamber to obtain the S-g-PMA resin (Figure 2) of moisture level 15–20%.

Both twin screw and single screw extruders were employed for the loose fill foam production. Screw configuration played an important role in the twin screw extruder for the starch-based loose-fill foam processing. The co-rotating and intermeshing twin screw extruder (Wegner TX 52) has a high shear design similar to that described by Lin and co-workers²¹ with a circulating oil heater. Water was injected into the barrel through a dual liquid pump as a lubricant and foaming agent. The S-g-PMA resin was fed using a twin screw volumetric feeder into the extruder and mixed with water in the feeding zone at a rate of 68 kg/hr. The temperatures were maintained throughout the experiment at 25, 30, 80, 130, 135, and 125 $^{\circ}\text{C}$, respectively, from the feeding zone to the

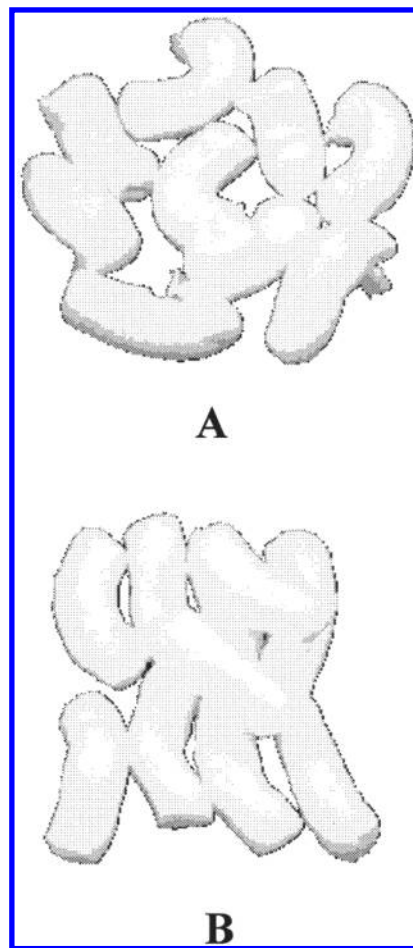


Figure 3. Starch graft poly(methyl acrylate) loose fill foam by (A) twin screw and (B) single screw extrusion.

die section. A one-hole die, tapered from 20 mm to 2 mm downstream through a distance of 20 mm, was used, and the extruder was operated at 200 rpm at a die pressure of 20.68 MPa. The extrudate expanded as it was forced out of the die and cut as a curved cylindrical shape (Figure 3A) using a six blade die face cutter with speed ranging from 200 to 350 rpm. The extrudate foams were collected and sealed in polyethylene bags and stored at room temperature for characterization.

The single screw extruder has higher conveying capability and can tolerate higher die pressure. Its weak mixing power can be compensated for by inserting mixing units into the screw configuration and operating at relatively higher die pressure and higher melting zone temperature. Production of S-g-PMA loose-fill foam is in principle similar to that of the twin screw extruder. The expanded foam is more stretched (Figure 3B) with about the same size as that from twin screw extrusion.

Physical Properties of S-g-PMA Loose-Fill Foams. Cell Sizes. Cell sizes of S-g-PMA loose-fill foams were determined by scanning electron micrographs in cross-section (Figure 4). Both twin screw (A) and single screw (B) extruders produced a uniform foam structure and open cells. However, the cell sizes for twin screw extrudates are twice as large as those from single screw extrusion, and the bulk density of the foam produced from twin screw extrusion is 25% heavier than that from single screw extrusion.

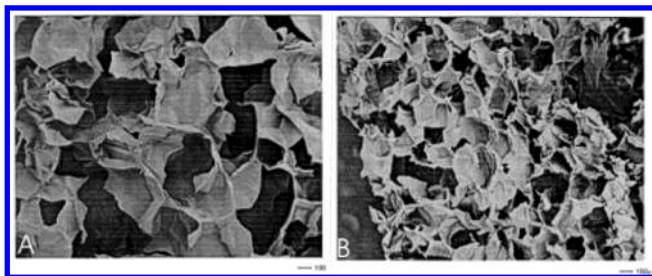


Figure 4. Scanning electronmicrographs of extruded S-g-PMA loose fill foam, twin screw (A) and single screw (B).

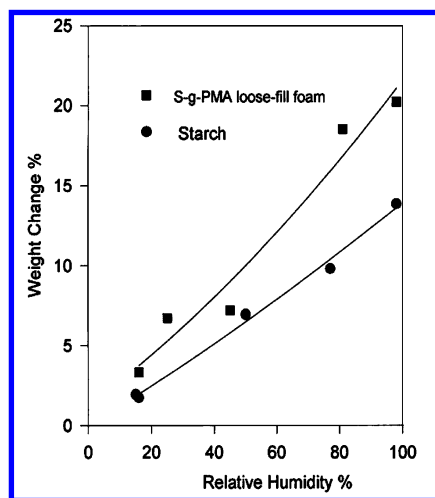


Figure 5. Weight change in S-g-PMA foam or starch as a function of relative humidity.

Table 2. Characteristics of Foams at 50% Relative Humidity

foam type	temp (°C)	compressive		resiliency (%)	bulk density (kg/m ³)
		strength (MPa)			
Pelaspan Pac	23	0.08 ± 0.02	79.32 ± 1.24	3.38 ± 0.12	
	35	0.07 ± 0.02	77.33 ± 0.88	3.42 ± 0.06	
Flo-Pak	23	0.05 ± 0.00	82.70 ± 1.02	3.51 ± 0.08	
	35	0.04 ± 0.00	78.91 ± 4.09	3.76 ± 0.08	
S-g-PMA	23	0.07 ± 0.01	70.17 ± 1.35	8.59 ± 0.21	
	35	0.08 ± 0.02	70.69 ± 1.20	8.91 ± 0.17	

Moisture Absorption. Moisture absorption of S-g-PMA was determined by weight changes after loose-fill samples were equilibrated in humidity controlled chambers for over one week. Similar to starch itself, the moisture absorption for S-g-PMA foam increased as the relative humidity increased. S-g-PMA loose-fill foam samples exhibited higher moisture absorption capability than starch granules (Figure 5) in the humidity range studied. As starch granules were destroyed during foam processing under high shear, more hydrophilic carbohydrate surface was exposed to the environment and higher moisture content was observed. This result is consistent with the moisture sorption isotherm of extruded starch foam reported by Lin et al.²¹

Physical Properties. Physical properties of loose-fill packaging materials are usually characterized by their compression strength, resiliency, water resistance, and bulk density. As shown in Table 2, Cunningham and Tatarka²⁵ found that at 50% relative humidity S-g-PMA has a compressive strength comparable to virgin expanded polystyrene foam (Pelaspan Pac) and recycled polystyrene foam

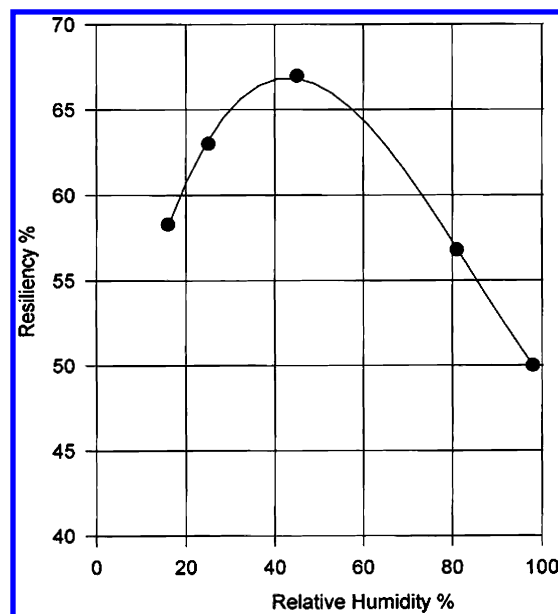


Figure 6. Resiliency of starch poly (methyl acrylate) foam at variable relative humidity.

(Flo Pak). The resiliency of S-g-PMA foam is not as high as that of expanded polystyrene but is normally considered good enough in the packaging industry for practical purposes. The bulk density of S-g-PMA foam, like other commercial starch-based foams,¹⁴ is much higher than expanded polystyrene foam and needs to be improved for reduction of shipping costs.

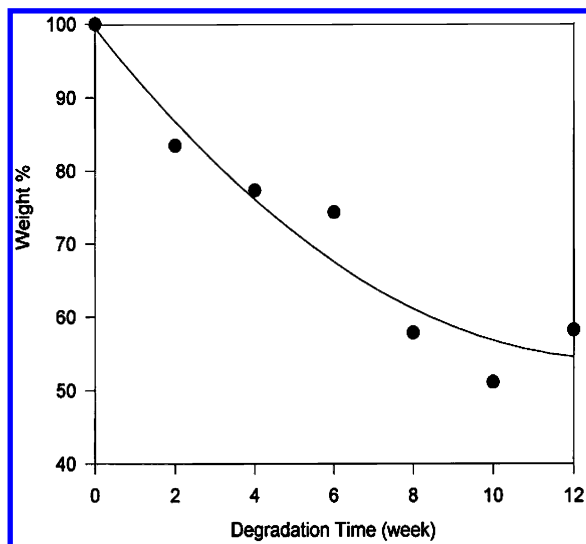
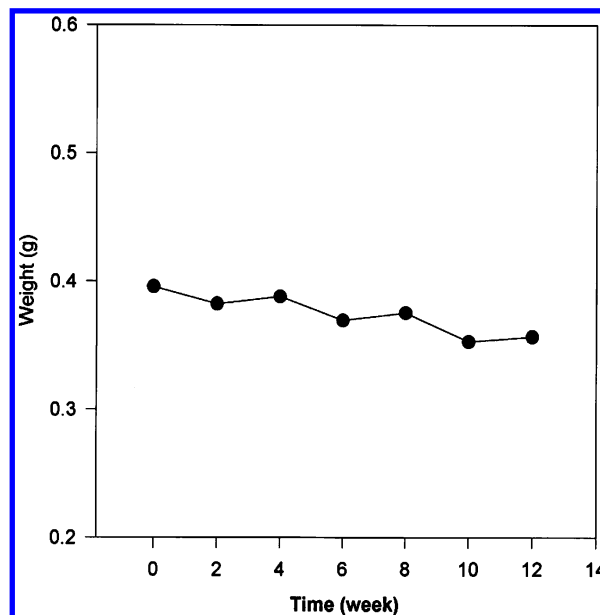
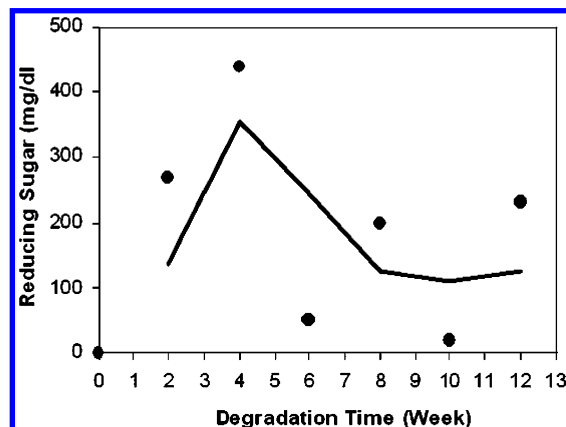
The resiliency of starch-based loose-fill foam is also related to the humidity in the environment. As indicated in Figure 6, S-g-PMA performed best when the relative humidity was within the 30–55% range with resiliency above 60%. Increasing humidity significantly decreased the resiliency, whereas under very dry conditions, the S-g-PMA became brittle. After conditioning under extreme high humidity, when the S-g-PMA foam was stirred in water, the foam shrank but still remained intact within 30 min, whereas other starch-based foams disintegrated relatively fast (Table 3). This property implied that S-g-PMA loose fill foams are more suitable for applications in a wide range of weather conditions.

Biodegradation of S-g-PMA Loose-Fill Foams. Starch is a well-known naturally produced polymer that is biodegradable in the natural environment. As synthetic polymer was grafted onto starch and the material was processed under high pressure and high shear, the starch granule structure was destroyed and its biodegradability might also have been altered. On the other hand, poly(methyl acrylate) is not a biodegradable polymer by itself. It was not clear whether the overwhelming presence of incorporated starch can assist microorganisms to attack poly(methyl acrylate) when the graft level was low (less than 10%).

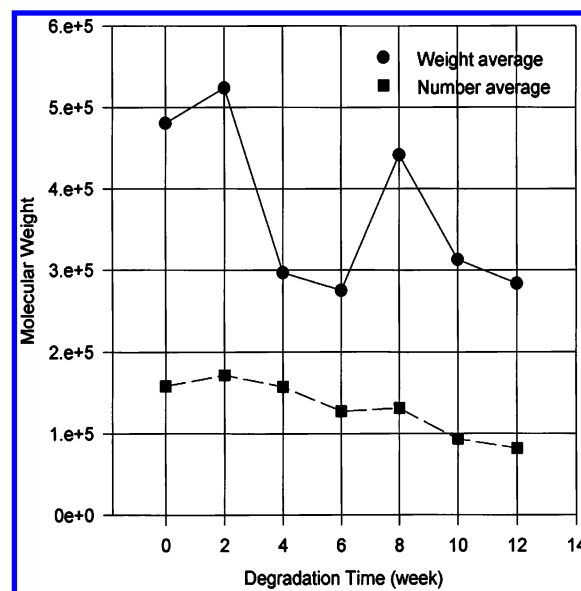
S-g-PMA loose-fill foam was soaked with water containing a laboratory consortium of highly amylolytic microorganisms designated as LD 76¹⁷ at constant temperature. Triple samples were removed every two weeks and analyzed for weight loss, reducing sugar content, and poly(methyl acrylate) content and molecular weight. The total weight lost for S-g-PMA foam is expressed in Figure 7 as the decreasing weight%

Table 3. Water Sensitivity Test for Starch-based Loose-Fill Foams

product name	manufacturer	start disintegration time (min)	complete disintegration time (min)
Eco-Foam	National Starch	1.0	1.5
Clean Grean	Clean Grean	2.2	3.0
EnPac	EnPac	1.0	2.0
Star Kone (S-g-PMA)	Uni-Star	shrunken but not disintegrated after 30 min	

**Figure 7.** Starch graft poly (methyl acrylate) weight loss in aqueous medium.**Figure 9.** Weight loss in poly(methyl acrylate) foams in time.**Figure 8.** Release of reducing sugars as a function of biodegradation in time from starch graft poly(methyl acrylate) foam.

over 12 weeks. About 50% of the S-g-PMA foam was consumed by microorganisms or became small fragments soluble in water within the 12 week period. It was noticed that not only microorganisms LD 76 degraded the S-g-PMA but a contamination by nature on the foam itself also produced fungi inside the test flask and competed in the biodegradation. To probe the degradation products, a reducing sugar assay method was utilized on a solution of the degraded mixture. As indicated in the Figure 8, a large amount of reducing sugar was produced for the first four weeks and then it dropped and varied randomly at lower levels. One possible explanation for this is that, at the beginning of biodegradation, more fragments of starch with reducing sugar terminals were generated than consumed by microorganisms or fungi. As high molecular weight starch became less available, more fragments were digested and the number of reducing sugar fragments declined.

**Figure 10.** Changes in the molecular weight of foam material during degradation.

The weight change of poly(methyl acrylate) from degraded S-g-PMA foam is illustrated in Figure 9. No appreciable weight loss was observed although the overall trend implied a decrease in the poly(methyl acrylate). This observation may be attributed to two factors: partial hydrolysis of methyl ester groups during the degradation and chemical isolation and incomplete separation due to experimental difficulty. The molecular weight average (M_n) from the degraded mixture appeared slightly decreased over time (Figure 10) for poly(methyl acrylate), which might result from hydrolysis of

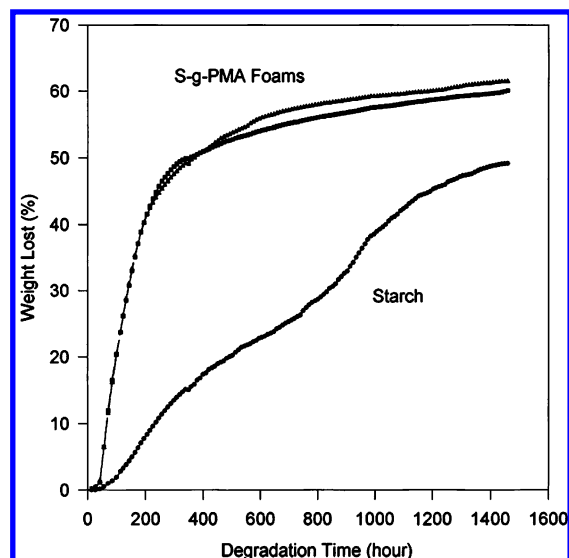


Figure 11. Weight losses for foam and starch during degradation in soil.

methyl ester groups. However, it should be pointed out that, because of the small amount of sample and limited accuracy of GPC, the decrease of poly(methyl acrylate) weight and its molecular weight may not be significant statistically, and a longer degradation period and more accurate assay method may be required for this study.

When S-g-PMA loose-fill foam was buried in soil, its biodegradation was monitored using a computer controlled close circulated respirometer. The concentration of carbon dioxide in each sample chamber was periodically analyzed and accumulated to give the total volume. The volume of carbon dioxide was converted to weight change (%) assuming that all starch digested by microorganisms was completely converted to carbon dioxide. Figure 11 shows the net weight changes (sample minus soil background) for starch and for two S-g-PMA foam samples. It is obvious that in the soil burial condition S-g-PMA degradation was much faster than ungrafted starch at the beginning and slowed after 200 h. Almost 50% of the weight was consumed within 250 h and more than 60% of the weight was degraded over 1450 h. This degradation pattern revealed that S-g-PMA loose-fill foam has more accessible carbohydrate surface and the carbohydrate portion can be biodegraded much faster.

Conclusions

Starch graft poly(methyl acrylate) resin and loose-fill foam have been prepared using prime starch as the feeding material in pilot scale. The graft polymerization process was modified, and the final products were made by twin screw or single

screw extrusion. The physical properties of these products indicated that S-g-PMA loose-fill foam has compressive strength and resiliency comparable to expanded polystyrene but higher density. S-g-PMA loose-fill foam has better moisture and water resistance than other starch-based materials. Biodegradation studies indicated that the starch portion in S-g-PMA loose-fill foam degraded fast while poly(methyl acrylate) remained relatively stable.

Acknowledgment. The authors thank Ms. Jan V. Lawton for the biodegradation and analytical assistance, Mr. F. Lee Baker for scanning electron microscopy, Dr. Jeffery A. Ahlgren and Mr. James J. Nicholson for their assistance in reducing sugar analysis and in computer graphics generation. Some of the material processing was done at then Unistar Industry located in Canton, Illinois.

References and Notes

- (1) Griffin, G. J. L. U.S. Patent 4,016,177, 1977.
- (2) Griffin, G. J. L. U.S. Patent 4,021,338, 1977.
- (3) Griffin, G. J. L. U.S. Patent 4,125,495, 1977.
- (4) Otey, F. H.; Westhoff, R. P. U.S. Patent 4,133,784, 1979.
- (5) Otey, F. H.; Westhoff, R. P. U.S. Patent 4,337,181, 1982.
- (6) Otey, F. H.; Westhoff, R. P.; Doane, W. M. *Ind. Eng. Chem. Res.* **1987**, 26, 1659.
- (7) Swanson, C. L.; Shogren, R. L.; Fanta, G. F.; Imam, S. H. *J. Envir. Polym. Degrad.* **1993**, 1, 155–165.
- (8) Lay, G.; Rehm, J.; Stepto, R. F.; Thom, M.; Sachetto, J.-P.; Lentz, D. J.; Silbiger, J. U.S. Patent 5,095,054, 1989.
- (9) Bagley, E. B.; Fanta, G. F.; Doane, W. M.; Gugliemelli, L. A.; Russell, C. R. U.S. Patent 4,026,849, 1977.
- (10) Trimnell, D.; Swanson, C. L.; Shogren, R. L.; Fanta, G. F. *J. Appl. Polym. Sci.* **1993**, 48, 1665.
- (11) Bagley, E. B.; Fanta, G. F.; Burr, R. C.; Doane, W. M.; Russell, C. R. *Polym. Eng. Sci.* **1977**, 17, 311.
- (12) Dennenberg, R. J.; Bothast, R. J.; Abbott, T. P. *J. Appl. Polym. Sci.* **1978**, 22, 459.
- (13) Fanta, G. F.; Doane, W. M. In *Modified Starches: Properties and Uses*; Wurzburg, O. B., Ed.; CRC Press: Boca Raton, FL, 1986; p 151.
- (14) Swanson, C. L.; Fanta, G. F.; Bagley, E. B. *Polym. Compos.* **1984**, 5, 52.
- (15) Henderson, A. M.; Rudin, A. *J. Appl. Polymer Sci.* **1982**, 27, 4115.
- (16) Henderson, A. M.; Rudin, A. *Angew. Makromol. Chem.* **1992**, 194, 23.
- (17) Liu, M.; Cheng, R.; Wu, J.; Ma, C. *J. Polym. Sci.: Part A: Polym. Chem.* **1993**, 31, 3181.
- (18) Patil, D. R.; Fanta, G. F. *Starch* **1995**, 47, 110.
- (19) Fanta, G. F.; Otey, F. H. U.S. Patent 4,839,450, 1988.
- (20) Tatarka, P. *The Plastics Challenge—A Revolution in Education*; SPE 53rd Annual Technical Conference & Exhibits: 1995; p 2225.
- (21) Lin, Y.; Huff, H. E.; Parsons, M. H.; Iannotti, E.; Hsieh, F. *Food Sci. Technol.: Lebesm.-Wiss. u.-Technol.* **1995**, 28, 163–168.
- (22) Shogren, R. L. *Carbohydr. Polym.* **1996**, 29, 57–62.
- (23) Gould, J. M.; Gordon, S. H.; Dexter, L. B.; Swanson, C. L. *Agricultural and Synthetic Polymers: Biodegradability and Utilization*, ACS Symposium Series No. 433; American Chemical Society: Washington, DC, 1990; Chapter VII.
- (24) Mino, G.; Kaizerman, S. *J. Polym. Sci.* **1960**, 31, 242.
- (25) Cunningham, R. L.; Tatarka, P. D. Private communication, 1996.

BM0344102